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Understanding surface and interfacial properties remains a challenging task, particularly when these interfacial regions are under relatively reactive conditions. This is particularly true of semconductor surfaces which can be highly reactive under ambient or processing conditions. One of the studies to be described in this presentation is our recent work on Si electrode surfaces. In recent years significant progress has been made in characterizing the Si/electrolyte interface by infrared reflectance, ultra-high vacuum UHV transfer experiments, and scanning tunneling microscopy STM and AFM imaging. These studies have taken advantage of the relative stability of Si surface prepared in a hydrogen terminated state. The more usual form in either air or in water is a heavily oxidezed Si surface for which much less is known because of the inapplicability of many of the above techniques to examining the Si/SiO_2 interfacial region. The presence of the oxide can significantly alter the electrochemistry and the electronic properties of the semiconductor. In this paper we discuss our application of optical second harmonic generation (SHG) to studying the Si/electrolyte and Si/SiO_2/electrolyte interfaces for which oxides ahve been photoanalytically grown on the surface.

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APPLICATION OF OPTICAL SECOND HARMONIC GENERATION TO SURFACE ANALYSIS

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Understanding surface and interfacial properties remains a challengeing task, particularly when these interfacial regions are under relatively reactive conditions. This is particularly true of semiconductor surfaces which can be highly reactive under ambient or processing conditions. One of the studies to be described in this presentation is our recent work on Si electrode surfaces. In recent years significant progress has been made in characterizing the Si/electrolyte interface by infrared reflectance [1, 2], ultra-high vacuum UHV transfer experiments, and scanning tunneling microscopy STM and AFM imaging.[3-6] These studies have taken advantage of the relative stability of Si surfaces prepared in a hydrogen terminated state. The more usual form in either air or in water is a heavily oxidized Si surface for which much less is known because of the inapplicability of many of the above techniques to examining the Si/SiO_2 interfacial region. The presence of the oxide can significantly alter the electrochemistry and the electronic properties of the semiconductor. In this paper we discuss our application of optical second harmonic generation (SHG) to studying Si/electrolyte and Si/SiO_2/electrolyte interfaces for which oxides have been photoanalytically grown on the surface. Second order nonlinear optical methods such as SHG and sum-frequency generation (SFG) are inherently sensitive to the properties of interfacial regions and have been used extensively for this purpose.[7-12] Although SHG and SFG have been used previously to examine Si(111) in UHV[13-15] and in air,[16, 17] application of these methods to this surface immersed and potentiostated in an electrolyte solution has been quite limited. This is understandable because of the complicated nature of the interfacial region and the reactive properties of the semiconductor electrode surface which make

it difficult to perform the fundamental SH studies necessary to set the stage for the application of the technique to analytical problems.

There have been two primary objectives in this study. The first has been to determine if the intensity and phase of the SH optical response is sensitive to potential induced variations in the static field applied to the semiconductor/electrolyte interface, and related to this, how the presence of oxide layers of varied thicknesses on the Si(111) surface alters this potential dependence. Because semiconductors can have a relatively large bulk response, it has not been clear whether any significant potential dependence can be observed from the semiconductor surface region. Unlike metal electrodes where SHG is highly sensitive to potential variation due to the screening of the charge at the surface,[7, 18] the field for semiconductors can extend several hundred angstroms into the material, the depth dependent upon the doping density of the semiconductor, possible Fermi level pinning and the strength of the applied field. Also of question is whether one can observe significant differences in the potential dependence between an oxide-free surface (in this case a H-terminated surface), and a surface with trace oxides present.

The second focus of our study has been of a more fundamental nature. That is, to address issues related to the source of the response from these buried interfaces including determining the coupling of the applied static field to various susceptibility tensors, and understanding the relative contribution from parts of the interfacial region such as the depletion layer, the Si(111) surface adjacent to the electrolyte or oxide, and the SiO_2 layer. Potential dependent measurements are an important means of examining such questions since the interfacial region can so readily be altered by simple potential variation.

To achieve our goals, we have examined H-Si(111) and the oxidized surface in different electrolyte solutions and in UHV. Much of the work reported has involved measuring the variation in the SH response with azimuthal rotation of the sample by 360°about its perpendicular axis. Such rotational anisotropy measurements which are conducted with selected input and output polarizations can provide valuable insight into the amplitude and phase of the

SH response as interfacial properties are altered. The simplest system is a H-terminated sample examined under potential control in NH_4F. This surface should be mono-hydrogen terminated, smooth and relatively free of any photogeneratued surface oxides due to the solubility the oxides in this basic solution. The SH rotational anisotropy from this surface has been examined for applied voltages within a selected potential range where the photocurrent is stable and the results are reproducible. A strong potential dependence in both the amplitude and the phase is observed from these samples. The results obtained at the flatband potential are compared with similar rotational anisotropy measurements conducted in UHV for a sputtered and annealed sample, and a hydrogen terminated sample examined in UHV without further surface cleaning. These studies are followed by potential dependent measurements of the SH rotational anisotropy from initially H-terminated surface in an H_2SO_4 solution where, unlike the NH_4F solution, the few monolayers of oxide which are formed photoanalytically on the surface do not dissolve. Similar experiments are conducted in H_2SO_4 on samples for which controlled amounts of surface oxides (0 - 40 Å) are photoanodically grown on the surface prior to examination of the SH potential dependence. A much different potential dependence in the phase and intensity of the SH response is observed relative to the H-Si.

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